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## Dual-Action Hygienic Coatings: Benefits of Hydrophobicity and Silver Ion Release and Surface Analysis

Niall Stobie

*Technological University Dublin*, [niall.stobie@tudublin.ie](mailto:niall.stobie@tudublin.ie)

Brendan Duffy

*Technological University Dublin*, [brendan.duffy@tudublin.ie](mailto:brendan.duffy@tudublin.ie)

John Colreavy

*Technological University Dublin*, [john.colreavy@tudublin.ie](mailto:john.colreavy@tudublin.ie)

Patrick McHale

*Technological University Dublin*, [patrick.mchale@tudublin.ie](mailto:patrick.mchale@tudublin.ie)

Steven Hinder

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*University of Surrey*, [S.Hinder@surrey.ac.uk](mailto:S.Hinder@surrey.ac.uk)

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**Authors**

Niall Stobie, Brendan Duffy, John Colreavy, Patrick McHale, Steven Hinder, and Declan McCormack



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## Dual-action hygienic coatings: Benefits of hydrophobicity and silver ion release for protection of environmental and clinical surfaces

Niall Stobie<sup>a,b,\*</sup>, Brendan Duffy<sup>b</sup>, John Colreavy<sup>b</sup>, Patrick McHale<sup>c</sup>, Steven J. Hinder<sup>d</sup>, Declan E. McCormack<sup>a</sup>

<sup>a</sup>School of Chemical and Pharmaceutical Sciences, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland

<sup>b</sup>Centre for Research in Engineering Surface Technology (CREST), FOCAS Institute, Dublin Institute of Technology, Dublin 8, Ireland

<sup>c</sup>School of Biological Sciences, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland

<sup>d</sup>The Surface Analysis Laboratory, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, Surrey GU2 7XH, UK

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### ABSTRACT

Coatings that demonstrate reduced attachment of crystalline precipitates and the medical device colonising *Staphylococcus epidermidis* were prepared by the immobilisation of silver doped perfluoropolyether–urethane siloxane thin films on glass substrates. The presence of stratified hydrophobic perfluoropolyether groups protects the coating surface from the attachment of crystalline hydrophilic species such as chlorides and phosphates, whilst silver ion release inhibited attachment of *S. epidermidis* and subsequent biofilm formation *in vitro*. The release of silver ions protects the perfluoro groups from the hydrophobic interactions of *S. epidermidis* cells, which can reduce the hydrophobicity of the protective coating. These coatings also exhibited significant antibacterial activity against planktonic *Acinetobacter baumannii* and *S. epidermidis* bacterial strains. Detailed elemental and chemical surface analysis obtained using X-ray photoelectron spectroscopy (XPS) provided useful information on the effect of bacterial incubation on key indicator hydrophobic and hydrophilic functional groups. XPS analysis indicated preferential adsorption of *S. epidermidis* cells at the hydrophobic sites along the polymeric chain. These dual-action hygienic coatings can be employed to protect against contamination environmental surfaces and bacterial colonisation on implanted medical devices.

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### 1. Introduction

There is mounting evidence that environmental and clinical surfaces that harbour bacteria, can become sources of healthcare-associated infections (HCAI) [1]. Bacteria such as staphylococci have been reported to survive on surfaces outside the human host, over a range of temperatures and conditions for time periods ranging from 3 months to 5 years [2]. Methicillin-resistant *Staphylococcus aureus* (MRSA) has been reported to persist on surfaces even after steam cleaning and chlorine biocide treatment [2,3]. Inanimate objects such as computer keyboards, door handles, telephones, hand-rails and bedside tables can harbour bacteria after human contact leading to contaminated surfaces [4,5]. In addition, the presence of moist environments will favour surface bacterial proliferation [6]. The transmission of pathogenic bacteria by hand contact with environmental surfaces is not solely limited to the

healthcare setting but can occur on environmental surfaces on public transport and in sports facilities and other communal areas.

A recent report published by the Royal College of Physicians of Ireland indicated that between 5% and 10% of patients admitted to hospitals will develop healthcare associated infections (HCAs), not all of which are preventable [7]. Risk factors for developing such infections include antibiotic usage, underlying medical conditions, surgery, catheterisation and non-compliance with hand disinfection protocols [8]. The colonisation of indwelling devices with adherent bacteria, such as *Staphylococcus epidermidis*, is one of the main factors in clinical device failure. This places a significant societal burden in terms of mortality, patient suffering and the associated financial cost. Free-floating bacteria are usually susceptible to antibiotics and phagocytes present in the body, but bacterial microcolonies, known as biofilms, have a propensity to resist the action of these agents [9]. The use of conventional antibiotic therapy is limited by both the increase in multi-drug resistant (MDR) bacteria and the inability of these agents to diffuse through the biofilm extracellular polymer matrix [10]. Moreover, sub-inhibitory doses of aminoglycoside antibiotics such as tobramycin have been reported to induce biofilm formation in *Escherichia coli* and *Pseudomonas aeruginosa* [11]. Implanted device coatings must function

\* Corresponding author. Address: Centre for Research in Engineering Surface Technology (CREST), FOCAS Institute, Dublin Institute of Technology, Dublin 8, Ireland.

E-mail address: niall.stobie@dit.ie (N. Stobie).

in a warm, saline-rich environment containing proteins and bio-macromolecules which can be contributory factors in oxidative damage on metallic implants [12]. Ionic species such as chlorides, present in aqueous environments, can also induce pitting corrosion on susceptible substrates [13].

Various strategies have been utilised in order to inhibit bacterial colonisation of surfaces such as modification of surface topography [9], direct coating of antibacterial agents onto surfaces [14] and tethering of polymeric biocides onto surfaces [15]. However such surfaces can become colonised and subsequently inactivated by physiological fluids [16]. In addition, the attachment of dead bacterial cells to implant surfaces may trigger adverse immunological responses [17]. One of the techniques proposed as a potential solution is the impregnation of surface coatings with antibacterial silver ions [16]. The increase in the use of silver doped antimicrobial devices and products can be attributed to a variety of factors including the broad-spectrum bactericidal activity of silver ions at low concentrations and the ability to inhibit bacterial attachment [18–20] with low cytotoxicity to normal mammalian cells [21]. Employing coatings with inherently self-cleaning or low surface energy properties provides an additional protective property to a surface. Low surface free energy coatings have demonstrated biofilm inhibition *in vivo* on intra-oral devices and urinary catheters, where varying shear forces predominate [22]. Perfluoropolyether (PFPE) based polymers are characterised by good chemical resistance, a low coefficient of friction and surface energy and are highly hydrophobic in nature [23–25]. Modification of these PFPE polymers with inorganic networks, such as silane functional groups, can yield hybrid coatings with interesting physical properties for antibacterial applications. Furthermore, segmented polyurethanes containing perfluoropolyether (PFPE) components demonstrated surface responsive behaviour upon immersion in water for potential use as antifouling coatings, where biofouling can be removed under shear-flow conditions.

In this current study, perfluoropolyether–urethane hybrid sol-gel coatings were employed as functional hosts for antibacterial silver ions. Several chemical methods for manufacturing antibacterial silver release coatings have been reported such as silver doped sol-gels and silver doped fluoropolymers. These coatings independently showed antibacterial activity but inorganic and organic

contamination was still observed after bacterial exposure [19,26]. In this work, biocidal silver ions and hydrophobic hybrid sol-gel coatings were combined to develop a dual-action hygienic coating for protection of surfaces against the precipitation of crystalline deposits and *S. epidermidis* colonisation. XPS analysis provided detailed information on the surface chemistry of the coatings before and after exposure to *S. epidermidis* broth. In particular, the effect of bacterial attachment on key indicator functional groups in the hybrid fluoropolymer coating was assessed. These dual action hybrid coatings may be applied onto short-term indwelling devices and inanimate surfaces in healthcare facilities and others communal sectors of interest.

## 2. Materials and methods

### 2.1. Experimental

In this work, perfluoropolyether–urethane hybrid coatings were prepared through a two-stage process. The first stage involved the reaction of a perfluoropolyether diol (Fluorolink D10-H, Solvay) with 3-isocyanatopropyltriethoxysilane (ICPTES, Aldrich) to generate the triethoxysilane terminated perfluoropolyether (Fig. 1). In a typical reaction, Fluorolink D10-H (10 g) was added to ICPTES (7.42 g) in the presence of a tin-free metal carboxylate catalyst (Borchi Kat 0245, 20 mg) and refluxed in a dry two-necked round-bottomed flask equipped with a condenser, thermometer port and a magnetic stirrer. This flask was immersed in a silicone oil bath maintained at 80 °C for 2 h under the presence of nitrogen. The molar ratio of the reactants were ICPTES:Perfluorinated diol (2.1:1). The progress of the reaction between the perfluorinated diol and the isocyanate functionalised alkoxy silane was monitored using Fourier-transform infra-red spectroscopy (FT-IR) in Attenuated Total Reflectance (ATR) mode by the disappearance of the isocyanate ( $\text{—N=C=O—}$ ) related peak at  $2260\text{ cm}^{-1}$  and the appearance of the urethane carbonyl ( $\text{—NH—(C=O)—O}$ ) related peak at approximately  $1720\text{ cm}^{-1}$  (Fig. 2). The resulting hybrid precursor was a slightly yellow colour. In the second stage, silver doped and undoped hybrid sols were prepared as follows: hybrid precursor (500  $\mu\text{l}$ ) was added to ethanol (10 ml) under magnetic

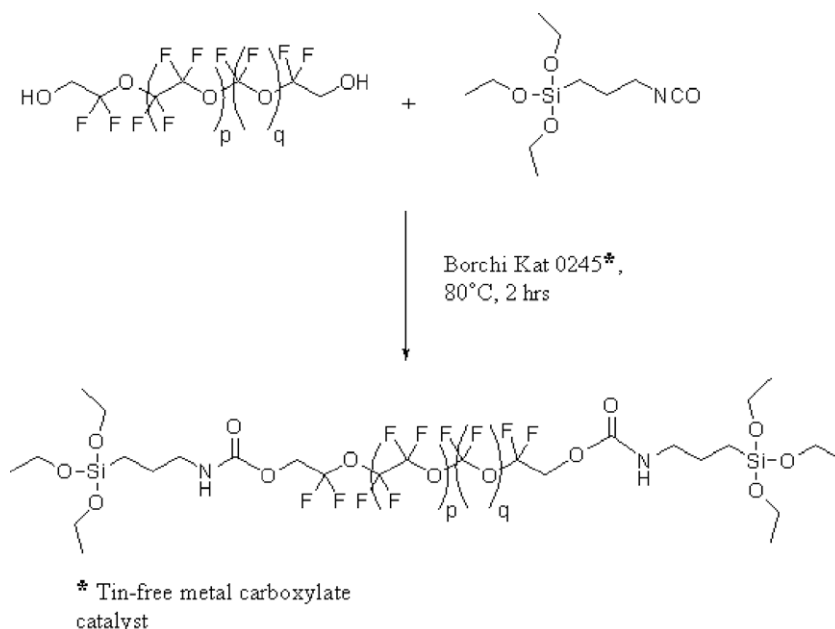
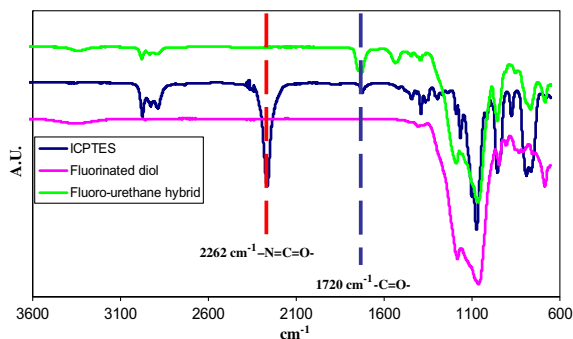


Fig. 1. Reaction scheme for perfluoropolyether–urethane siloxane polymer.



**Fig. 2.** FT-IR spectra of individual reactants and perfluoropolyether-urethane hybrid thin film after 2 h reaction time.

stirring. Water (2 mls) and 0.1 M  $\text{HNO}_3$  (500  $\mu\text{l}$ ) were slowly added to this solution and allowed to stir overnight. Silver doping was achieved by pre-dissolving silver nitrate (Aldrich, 50 mg) in water (2 mls). The resulting silver doped and undoped sols were spin-coated onto pre-cleaned glass substrates and allowed to cure at room temperature for 2 h, followed by 4 h at 100 °C to give nominal film thicknesses of approximately 3  $\mu\text{m}$ .

## 2.2. Instrumentation

The release of silver from the coatings was determined by Graphite Furnace-Atomic Absorption Spectroscopy using a Varian 110 Spectrometer equipped with a silver hollow cathode lamp. Microscopic analysis of the coatings was assessed using a Jeol 8600 scanning electron microscope (SEM). The samples were mounted on stubs and gold coated for SEM imaging at 15 keV. An X-ray Photoelectron Spectrometer (ESCALAB Mk II) equipped was used to analyse the surface composition of the undoped coatings and silver doped coatings. The instrument was equipped with a twin anode X-ray source (Al  $K\alpha$ /Mg  $K\alpha$ ) and an Alpha 110 analyser. Quantitative surface chemical analyses were calculated from the high resolution, core level spectra following the removal of a non-linear (Shirley) background. All binding energies were referenced to the hydrocarbon C1s peak at 285 eV to correct for electrostatic charging effects during acquisition. Sample mounting for XPS analysis was achieved by fixing a specimen to a VG sample stub using double sided adhesive tape. Contact measurements were obtained using an FTÅ Surface Energy Analyser.

## 2.3. Silver release

Coated glass pieces (25  $\text{cm}^2$ ) were immersed in physiologically buffered saline (PBS, 50 mls) initially for 1 h, followed by six succes-

sive 24 h immersion periods in fresh PBS. The resulting fluids were digested with concentrated nitric acid (0.5 ml) prior to graphite furnace analysis, to ensure dissolution of any silver based precipitates.

## 2.4. Antibacterial activity

The antibacterial activity of the silver doped and undoped coatings against planktonic *S. epidermidis* (CSF 41498) and *Acinetobacter baumannii* (clinical isolate) was determined using a modified version of the Japanese standard (JIS Z 2801). Stock cultures of the bacteria were grown on plate count agar (PCA-Oxoid) and sub-cultured overnight at 37 °C in nutrient broth to give a concentration of approximately  $10^8$  CFU/ml. This was diluted one in a hundred with maximum recovery diluent (MRD-Oxoid) to give working cultures of approximately  $10^6$  CFU/ml. Doped and undoped coated glass pieces (25  $\text{cm}^2$ ) were inoculated with 400  $\mu\text{l}$  of the bacterial cultures and incubated overnight. The coatings and bacterial suspensions were then agitated with MRD (20 mls) in sterile stomacher bags. The number of organisms released into the MRD was determined by plating serial tenfold dilutions onto PCA using the spread plate method and incubating overnight at 37 °C.

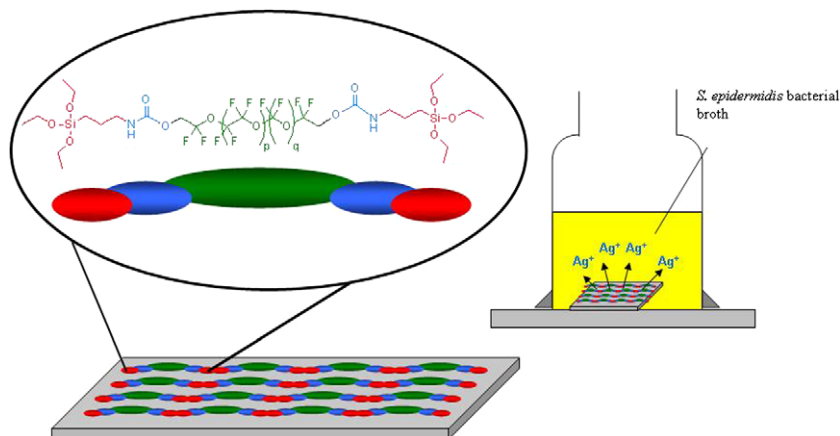
## 2.5. Biofilm growth

The ability of silver doped and undoped hybrid coatings to resist sessile bacterial colonisation was assessed using SEM and XPS analysis of the exposed surfaces. Gram-positive *S. epidermidis* was chosen as the test bacterium as it adheres and colonies implanted device surfaces. Coated glass pieces were immersed in a *S. epidermidis* broth culture (10 mls) of approximately  $10^6$  CFU/ml and incubated for 10 days at 37 °C (Fig. 3). The broth was removed and replaced with fresh sterile broth daily. This daily exchange of nutrient rich medium provided a useful method for challenging the antibacterial activity of the coating overtime. After incubation, the glass pieces were removed and gently rinsed twice with sterile water. The resulting samples were mounted on a stub and gold coated for SEM imaging at 15 keV. Detailed surface elemental and chemical composition of the silver doped and undoped hybrid sol-gel coatings was obtained using XPS.

## 3. Results and discussion

### 3.1. Silver release

Metal ion release from biomaterials is governed by numerous factors, including the amount of available surface silver, surface



**Fig. 3.** Surface immobilisation of perfluoropolyether hybrid sol-gel coating with active silver ion release.

functionality and the degree of hydrophobicity of the coating interface [27]. Furthermore, the area of the exposed coating and the volume of the neighbouring fluid will also influence release metal ion release. In particular, the presence of hydrophobic/hydrophilic groups at the liquid interface governs water permeation through the coating and subsequent silver ion release. In this work, the release of silver ions into PBS solution at 37 °C over 6 days is depicted in Fig. 4. During the first hour, approximately 200 ppb was released into the PBS, followed by a lower sustained release profile for 6 days – as determined by GF-AAS. It should be noted that this initial burst of silver ions would be beneficial in reducing the initial bacterial attachment, which is considered essential in preventing implanted medical device-associated infections [20]. A previous study of antibiotic-loaded bone cement exhibited *in vitro* release doses significantly higher than antibiotic resistance levels, for most bacterial strains causing implant-device infection [28]. The release of silver ions from a coating matrix is governed by species in the extraction media. In particular the minimum inhibitory concentration (MIC) of silver ions can vary significantly depending on the presence of chlorides and other biologically relevant anions and macromolecules [29]. The natural tendency of the PFPE segments to stratify to the air interface is predominantly driven by thermodynamic forces to minimise the surface energy and competition between migrating fluorinated molecules and the increasing viscosity as the curing temperature increases [23,30]. A previous study on fluorinated isocyanates indicated that the migration of fluorinated molecules to the air interface is retarded as the viscosity rises, and becomes practically impossible as the mixture solidifies [30]. In addition, the rapid evaporation of solvent from PFPE polyurethane electrospun fibres, as a result of aggregated chain conformation, led to depleted fluorine migration [31]. Lower processing temperatures retain the solvent for longer periods, resulting in enhanced stratification of PFPE segments. Therefore, in this study, the coatings were initially room temperature cured for 2 h, followed by a 100 °C processing step for an additional 4 h to remove residual ethanol and water for film formation. Indeed, it has been reported that low temperature processing retains surface silver in the upper layers of the sol–gel derived coatings, facilitating the release of biocidal silver ions into the surrounding medium [19]. High temperature processing of silver doped sol–gel systems leads to a diffusion of silver away from the surface and into the bulk. XPS analysis was employed to examine the surface of the silver doped hybrid sol–gel coatings before and after exposure tests. XPS is a useful analytical tool, which provides multi-element detection and quantification of surface contamination of biomaterials. There was a reduction in percentage atomic silver in the hybrid coatings, from 0.37% to 0.13% after the 6 day release into PBS (Fig. 5). Due to the presence of predominantly hydrophobic

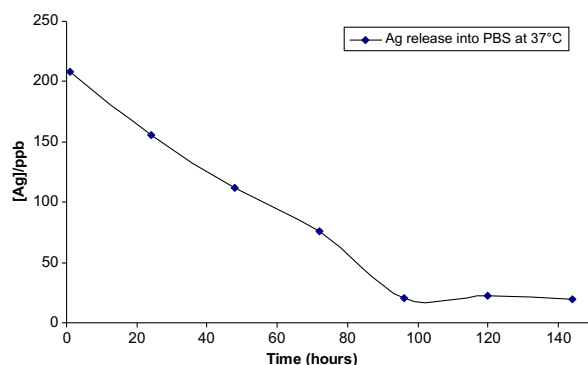


Fig. 4. Non-cumulative release of silver into fresh PBS medium from Ag doped coatings (determined by GF-AAS).

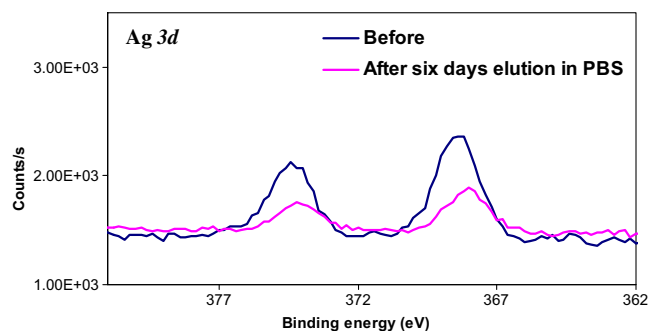


Fig. 5. Ag 3d XPS surface spectra of Ag doped fluoro hybrid coating before and after exposure to physiologically buffered saline at 37 °C for 6 days.

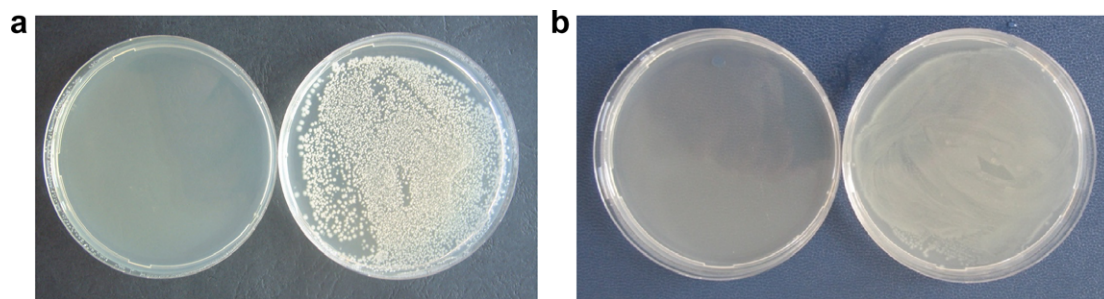
functional groups at the surface, it is plausible to suggest that the terminal urethane linkages on the PFPE segments provided a pathway for the diffusion of water molecules *via* dipole–dipole interactions and hydrogen bonding with the carboxyl functional groups. The ability of such PFPE–urethane based polymers to exhibit surface responsive behaviour in water has been previously demonstrated [19,25]. Whilst the antibacterial activity of silver ions may be reduced in a nutrient environment; antibacterial activity can still be observed by the slow release of silver ions from silver halide precipitates [32].

### 3.2. Antibacterial activity

Silver ions have shown broad-spectrum activity against pathogenic bacteria, including antibiotic resistant strains [19]. Reactive silver ions bind with and deactivate nucleophilic functional groups that are essential in bacterial processes. The release of silver ions from the perfluorinated coatings had a significant antibacterial effect against *S. epidermidis* (CSF 41498) and *A. baumannii* (clinical isolate). There was approximately 99% reduction in bacterial colonies on the silver doped hybrid coated pieces compared to the undoped coated pieces, following overnight incubation at 37 °C (Fig. 6). A comprehensive review on surface contamination and current antimicrobial coatings technologies has recently been published [33]. One strategy to inhibit surface colonisation is to render it antibacterial; either by direct coating or impregnation with antibacterial agents for active release into the neighbouring environment. One of the main benefits of silver ion impregnation is the ability to prevent the formation of bacterial conditioning films which render directly coated surfaces inactive [16]. These silver doped coatings can be applied to environmental surfaces and medical device coatings where bacterial colonisation may occur.

### 3.3. Biofilm growth

In biomedical and implant-device coatings, biomaterial surface chemistry is a key factor that influences initial bacterial attachment [34]. Biofilm formation is a multi-factorial process involving the adhesion of bacterial cells to a host substrate, followed by subsequent attachment and colonisation. *S. epidermidis* is the most frequently isolated bacteria from implant device related infections, as it colonises surfaces resulting in biofilm formation [35]. In biological systems, the interaction between *S. epidermidis* and surfaces is governed by hydrophobic interactions [36,37]. Whilst hydrophobic coatings may inhibit certain microbial interactions, such coatings are not effective against the initial attachment of *S. epidermidis* cells. In this work, we employed a coatings strategy that combined the benefits of antibacterial silver ions and hydrophobic chemistries to protect surfaces against the attachment of ionic precipitates and *S. epidermidis* colonisation. After *S. epidermidis* exposure

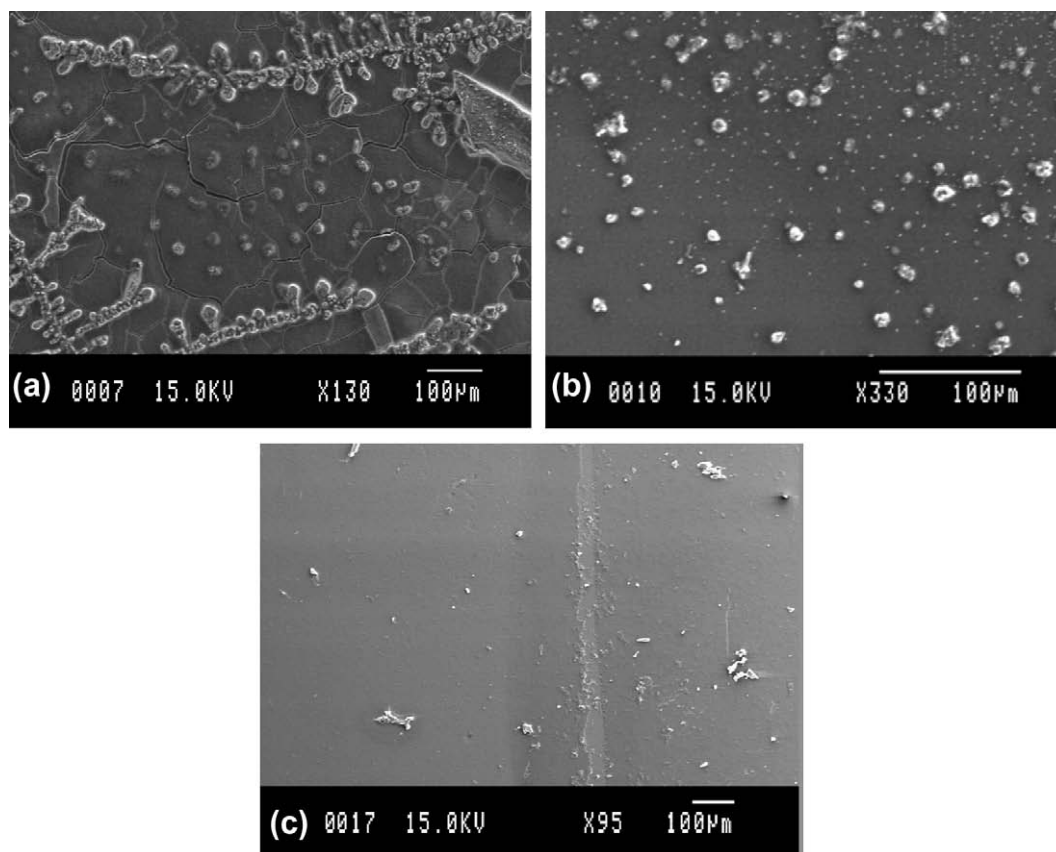


**Fig. 6.** Antibacterial activity of Ag doped hybrid sol-gel coatings against (a) *S. epidermidis* (CSF 41498) (b) *A. baumannii* (clinical isolate). Left plate: silver doped fluoropolymer. Right plate: undoped fluoropolymer (JIS Z 2801).

test, the bare glass substrate exhibited biofilm growth, predominantly on a base of adherent crystalline deposits (Fig. 7a). XPS analysis of the exposed glass substrate showed sodium, phosphorus and chlorine based species (Fig. 8).

*S. epidermidis* adsorption at hydrophilic surfaces, such as glass, is less likely due to preferential hydrogen bonding between water molecules and the surface [38]. As a result, the transport and adsorption of hydrophilic ionic species to the substrate will be the dominant process over *S. epidermidis* bacterial attachment. Hydrophobic surfaces have shown a greater affinity to fix *S. epidermidis* bacterial cells resulting in more immobile adhesion sites than on hydrophilic surfaces [39]. In addition, a previous study has all shown that extremely high fluid flows can stimulate the bacterial detachment of certain strains from surfaces. It was observed that fluid shear rates were effective in detaching hydrophilic bacteria over hydrophobic bacteria [40].

In contrast to the equivalent uncoated glass piece, SEM analysis of the fluorinated hybrid coating did not indicate the presence of crystalline deposits (Fig. 7b). XPS analysis did not detect any sodium, phosphorus, or chlorine based species. It can be concluded that the presence of hydrophobic PFPE segments at the air interface inhibited the attachment of ionic species present in the broth. (Fig. 7b). There was a decrease in the percentage atomic fluorine from 44.7% to 30.4% and a subsequent increase in the percentage atomic carbon content from 30% to 42% after 10 day incubation with *S. epidermidis* (Figs. 9a and 10a). The intensity of carbon and oxygen binding energies associated with  $-\text{CF}_2-\text{O}-\text{CF}_2-$  group decreased after *S. epidermidis* incubation (Figs. 10a and 11a) whilst there was no significant change in the binding associated with the hydrophilic urethane species  $-\text{NH}-(\text{C}=\text{O})-\text{O}-$ . These results indicate the preferential attraction of *S. epidermidis* cells towards the more hydrophobic sites.



**Fig. 7.** SEM images of (a) uncoated glass substrate, (b) fluoro hybrid coating and (c) silver doped fluoro hybrid coating following 10 days *S. epidermidis* broth culture incubation.

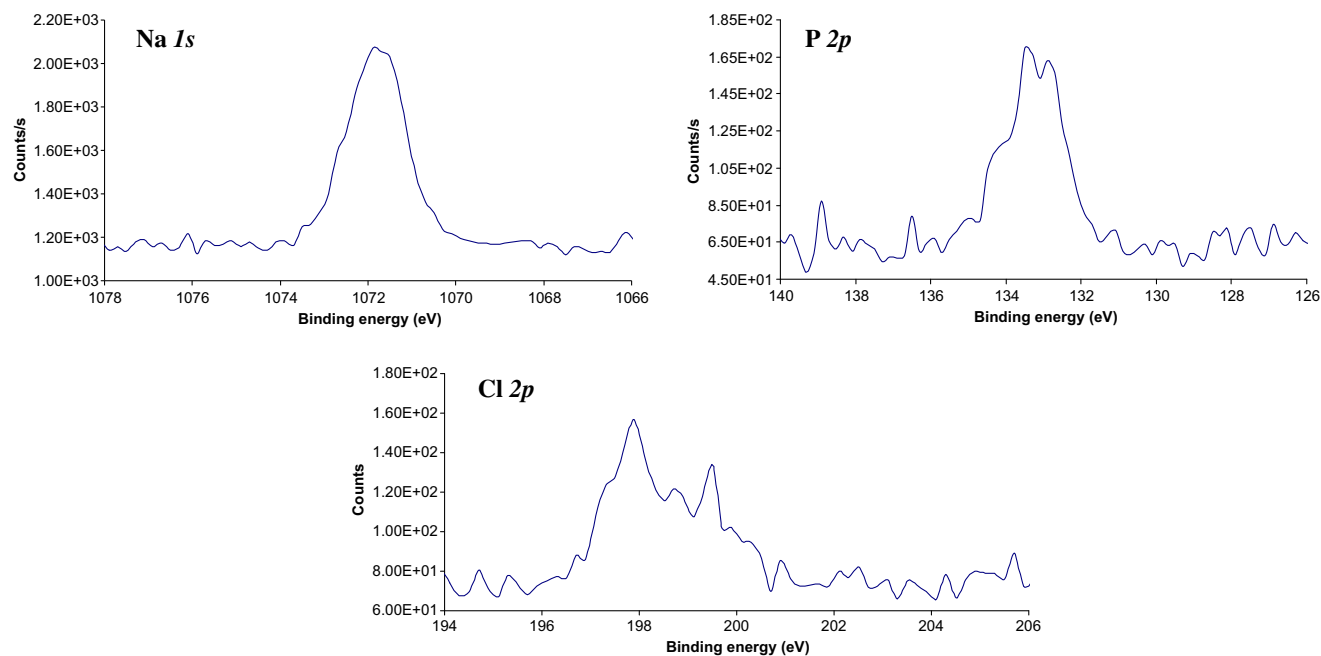


Fig. 8. Sodium, phosphorus and chlorine XPS analyses of glass surface following 10 days *S. epidermidis* broth culture incubation.

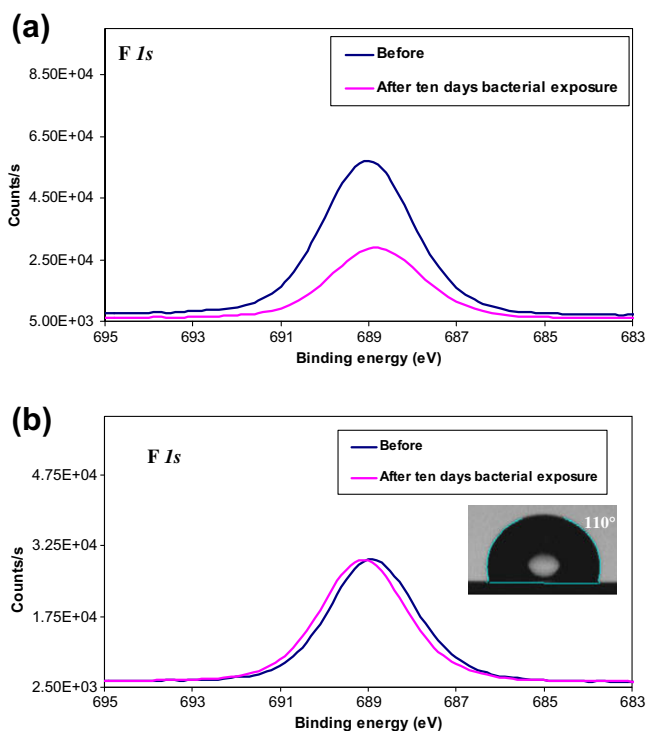


Fig. 9. F 1s XPS surface spectra of fluoro hybrid coating (a) and silver doped fluoro hybrid coating (b) before and after 10 days *S. epidermidis* broth culture incubation. Inset: contact angle measurement of fluorinated surface.

Silver ion release from the coatings reduced the adhesion of *S. epidermidis* bacterial cells, in comparison to the undoped perfluorinated hybrid coating. No significant reduction in binding energies was observed for elemental fluorine (Fig. 9b), carbon (Fig. 10b) or the carbon/oxygen components of the  $-\text{CF}_2-\text{O}-\text{CF}_2-$  functional groups (Figs. 10b and 11b), due to the protective antibacterial ef-

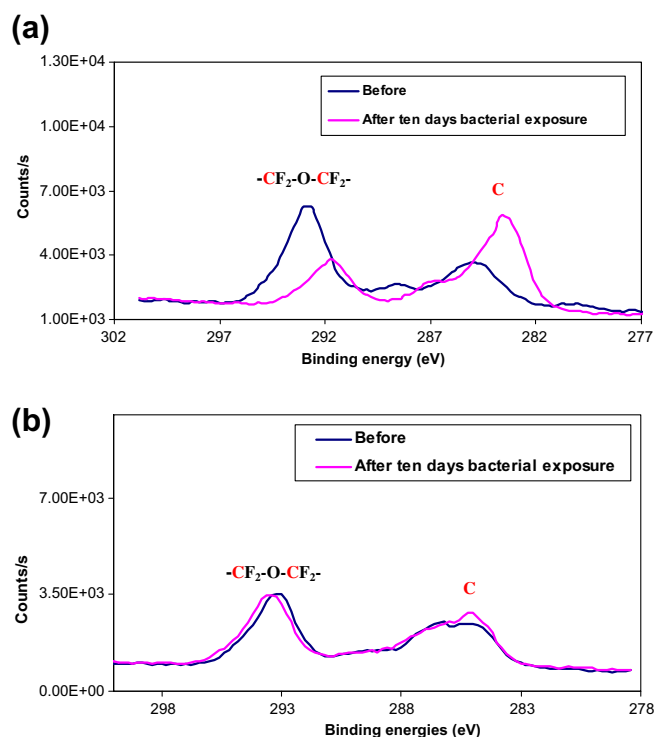
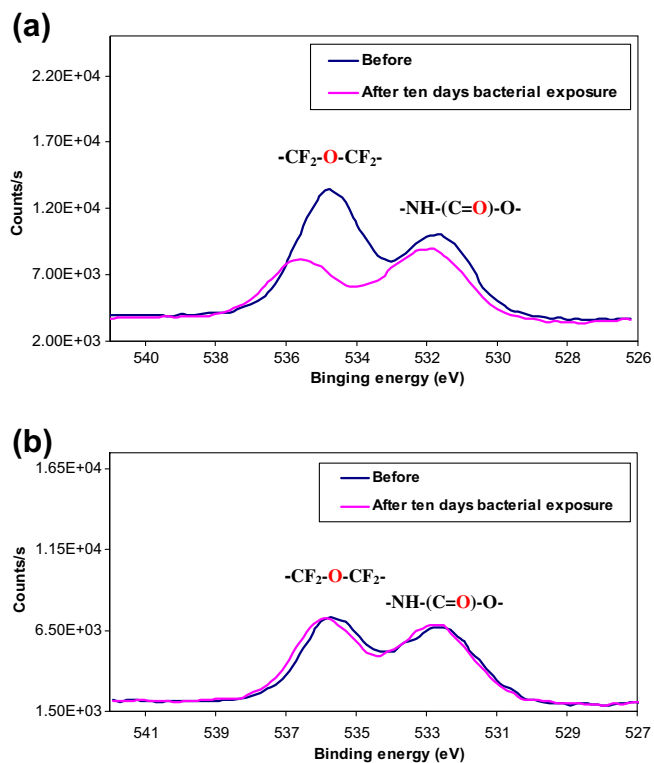


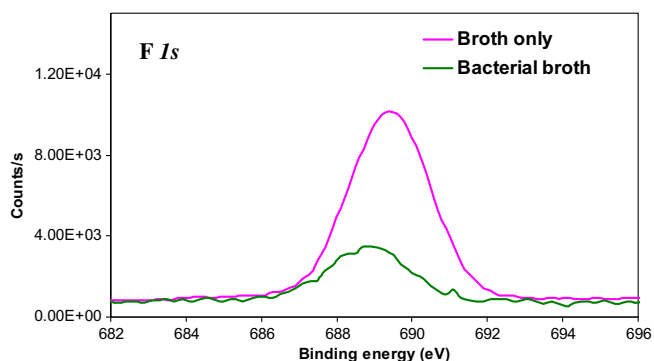
Fig. 10. C 1s XPS surface spectra of fluoro hybrid coating (a) and silver doped fluoro hybrid coating (b) before and after 10 days *S. epidermidis* broth culture incubation.

fect of the eluting silver ions. *S. epidermidis* broth exposure showed decreased surface fluorine intensity in comparison to the broth exposure alone; signifying the influence of hydrophobicity on *S. epidermidis* adhesion to the surface (Fig. 12). This reduction in the fluorine related binding energies suggested the preferential adsorption of *S. epidermidis* cells towards the hydrophobic sites along the polymeric chain. This information obtained by XPS is useful for screening the surfaces of potential biomaterials.





**Fig. 11.**  $1s$  XPS surface spectra of fluoro hybrid coating (a) and silver doped fluoro hybrid coating (b) before and after 10 days *S. epidermidis* broth culture incubation.



**Fig. 12.**  $1s$  XPS surface spectra of fluoro hybrid coating following 10 days *S. epidermidis* broth culture incubation and broth only incubation.

#### 4. Conclusion

Implanted biomaterial surfaces, including those coated with anti-infective agents, are vulnerable to colonisation by biofilm forming microorganisms. Furthermore, the ability of these pathogenic microbes to persist on environmental surfaces has led to the emergence of new antibacterial coating strategies. Dual-action hygienic coatings based on silver ion release from hydrophobic hosts are proposed as a potential solution to contamination on environmental and implanted surfaces. Silver ion elution from these hybrid coatings demonstrated significant antibacterial activity against planktonic *A. baumannii* and *S. epidermidis* strains. The antibacterial capacity of these coatings was challenged by the daily exchange of nutrient medium. The release of silver ions inhibited the attachment of *S. epidermidis* cells at the hydrophobic sites, where these hydrophobic sites protect the surface from the attachment of ionic species which can (a) deplete the available surface silver and reduce bio-activity (b) form crystalline precipitates

and salt deposits on susceptible substrates. Surface sensitive techniques such as XPS provided invaluable information on elemental and chemical compositions, by monitoring the effect of bacterial exposure on specific functional groups. In conjunction with complementary prophylactic and hygiene protocols, these dual-action hygienic coatings can be employed to provide protection on environmental and short-term indwelling surfaces where *S. epidermidis* colonisation can occur.

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